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Vol. 30. No. 246. June 1944.

PERMEATION OF HYDROCARBON GASES THROUGH RUBBER TUBING.

By M. J. Stross, J. L. Riley, and H. M. Eby.*

Introduction.

Gas permeation for planar films of rubber varies inversely with the thickness of the film and directly with the area. Likewise, permeation of gases through rubber tubing varies directly with the inside diameter and inversely with the wall thickness. For each type of rubber tubing the rate of permeation of different gases varies over a wide range. In general, monoolefins permeate rubber more rapidly than paraffins. The hydrocarbons of the C_4 group permeate rubber tubing much more rapidly than those of lower molecular weight, and the normal hydrocarbons more rapidly than branched isomers.

Synthetic rubber tubing—*e.g.*, Neoprene and particularly Koroseal—are much less permeable than compounds of natural rubber. Plastic tubings such as Resistoflex are much superior in this respect to either synthetic or natural rubber, but are limited in application because of their solubility.

Permeability.

Historical Survey.

As early as 1866, Graham [1] first reported that rubber membranes are permeable to gases. He showed that this permeation takes place by solution of the gas in the rubber. Correlation of density or viscosity of the gases with the rate of penetration indicates that these properties could not be used for this evaluation. Edwards and Pickering [2] show that the rate of penetration of a given gas is directly proportional to the difference in partial pressure of that gas on the two sides of the membrane, and that the rate increases rapidly with the temperature.

Venable and Fuwa [3] studied the solubility of gases in rubber and rubber stock, and the effect of solubility on penetrability. They found that (*a*) when rubber absorbs a gas, the gas is held in true solution, and not by adsorption; (*b*) carbon dioxide in solution is proportional to pressure, and is independent of degree of vulcanization or the presence of compounding ingredients; (*c*) solubility decreases rapidly with increasing temperature; (*d*) relative solubility values obtained for various gases show that there is a general relation between solubility and density of a gas and the rate of penetration through rubber. The size and structure of the gas molecule and the viscosity of the rubber likewise markedly influence this rate of penetration, and in a predictable direction.

Dewar,[4] in studying the rate of diffusion of gases through india-rubber, found that the rate increases rapidly with rise of temperature. When he

* Universal Oil Products Company.

plotted the logarithms of the rates against temperatures he obtained straight lines (Log R vs kT) with breaks at 0° C., indicating influence of water, and a much more pronounced break for carbon dioxide at −37° C.

Barrer [16] developed the theoretical basis for the permeation of rubber membranes by gases which he sought to relate to diffusion of gases in liquids. He related his permeability constant, P, in c.c. at N.T.P. diffusing per second through unit area (1 cm.^{2}) of a membrane 1 mm. thick, when there is a centimetre of mercury difference in pressure between its faces to the diffusion constant, D, in c.c. at N.T.P. diffusing per second through a 1-cm. cube within the solid when there is unit concentration gradient across the cube (cm.^{2} sec.$^{-1}$) and the solubility constant σ in c.c. at N.T.P. per cm.^{3} of solid when pressure is one atmosphere in the expression $P = \frac{-D\sigma\Delta P}{l}$ (for steady state of flow), where ΔP is the difference in pressure and l is the thickness of the membrane. This is Ficks' law of diffusion and is applicable when the solubility obeys Henry's Law, $C = \sigma P$.

As a finite length of time is required to achieve the steady state of flow Daynes [17] related D to L, the time lag required to achieve the steady state of flow in the expression $L = \frac{l^2}{6D}$. Barrer used this expression in evaluating D from experimental work. P was determined directly, and solubility was calculated from the expression $P = \frac{-D \cdot \sigma \cdot \Delta P}{l}$.

Davey and Ohya [5] studied the influence of compounding ingredients on the permeability of rubber to gases. Permeability is lower in accelerated than in unaccelerated mixtures, is still further lowered by antioxidants and plasticizers, but is increased by mineral fillers, and is lower before curing than after. Morris [7] states that permeability varies inversely with the thickness of the rubber and with the volume of compounding ingredients. It varies little or not at all with milling, type of crude, and temperature of vulcanization. Permeability has a minimum as a function of curing time.

Alexejev and Matalskii,[6] studying mixtures of gases, showed that the diffusion velocity of a mixture is equal to the sum of the diffusion velocities of its components, even for individual differences in value of the latter and wide range of composition in the mixture.

Kanata [15] determined the relative permeabilities of rubber, gelatin, and celluloid for several gases, and Sager [9, 13] determined the hydrogen and helium permeabilities of a wide range of organic resins, including two synthetics. Drinberg [8] presents the order of hydrogen permeability of various lyophilic colloids. He found that depolymerization increases permeability, while water absorption and solvation decrease it. Morris and Street [10] found that the permeability of rubber by air is increased by long immersion in water.

Williams and Neal [11] found that at constant temperature (29° C.) the solubility of oxygen in rubber is proportional to pressure from 193 mm. to 1538 mm. of mercury. Up to 30° C., solubility decreases with increase in temperature, and above 40° C. increases with increase in temperature, as the result of oxidation of the rubber.

Branham [14] studied the sources and extent of errors in gas analysis.

His investigation covered both permanent and temporary loss of gas sample in the apparatus by absorption in exposed rubber tubing and stopcock grease. In permanent loss the sample escapes to the air. In temporary loss it is returned to the gas chamber when a gas of low partial pressure in the " lost " constituents is inserted.

The greater part of the work done by these investigators was done with hydrogen, helium, oxygen, and nitrogen, the two former gases being of interest in balloon construction and the two latter in the ageing of rubber. The hydrocarbon gases have been largely neglected. All previous results have been reported for flat sheets of rubber, and it is doubtful whether these results are interpretable for annular sections of material. No such calculations have been reported in the literature.

Many directions for gas analysis include precautions against the use of rubber tubing in the course of the analysis or as a carrier of gases to be analysed; but prior to 1934 [14] no one reported on the possible magnitude of the effect. One of the purposes of the present work was to determine, for gases commonly dealt with in petroleum technology, how much loss and change of composition occur for any gas or gas mixture in contact with a known amount of rubber tubing.

Apparatus and Procedure.

The apparatus consisted of a standard gas analysis burette, to which was connected, by rubber tubing, a levelling bottle containing retaining solution. This solution, which was made by saturating distilled water with sodium sulphate, was slightly acidified and was degassed by pumping out at room temperature. The piece of rubber tubing to be tested was attached securely to the left lead of the burette stopcock. Tubing samples varied in length from 10 to 20 inches.

Gas samples were stored in clean glass sample tubes. The nipples on the ends of the sample tubes were kept filled with water as an added precaution against leakage. Degassed distilled water was used to displace the gas from the storage tubes, and pressure in the tubes was maintained slightly above atmospheric. The gases were taken from steel cylinders and their purities were indicated as follows: *iso*butylene, 98 per cent.; normal butylene, 99 per cent.; *iso*butane, 100 per cent.; normal butane, 100 per cent.; it was found early in the course of the experiments that most of the pure and C.P. gases used contained traces of impermeable components, which were usually found to be inerts.

The extreme end of the test sample of rubber tubing was connected to an efficient vacuum pump, evacuated, and closed by means of a screw-clamp. A connecting line between the burette and gas-sample tube, consisting of glass and Neoprene tubing, was filled with retaining solution. A levelling bottle, filled with freshly boiled distilled water, was connected to the lower stopcock of the gas-sample tube. A volume of gas equal to 100 ml. plus the internal volume of the rubber tube was taken into the burette. The liquid level in the levelling bottle was kept at the level of the solution in the burette. A reference burette, containing air served as a correction for change of volume due to changes in barometric pressure and temperature.

Each experiment was started by turning the burette stopcock in such a

manner as to introduce the gas into the rubber tubing. The contact period was timed with a stopwatch. Readings were taken at 1-minute intervals for 5 minutes, and at 4-minute intervals thereafter. Four units were operated simultaneously, using similar tubing and four different gases. The reference burette was observed with each test observation and proper volume corrections made.

Scope of the Investigation.

Samples of every type of natural and synthetic rubber tubing available at these laboratories were used in this programme. The gases for the tests were analyzed by fractionation on Podbielniak fractionating equipment and by chemical absorption in accordance with the methods described in the 1940 edition of the U.O.P. Methods Book.

A single type of tubing, Adams Supreme Pure Gum Rubber Tubing, 4 mm. I.D., 7½ mm. O.D., was tested with a series of thirteen gases. The results are tabulated in Table I, which gives an indication of the extent to which these gases permeate gum-rubber tubing, and affords a means of comparing the present work with that of earlier workers on sheet rubber with hydrogen, helium, and the atmospheric gases.

Each of the samples of tubing used was weighed empty, then filled with water, weighed, and the specific gravity determined. From these data and from the length of the tubing were calculated the following: (1) the inside diameter, (2) the outside diameter, (3) average wall thickness, and (4) the internal area. Direct measurements of these dimensions would have introduced much larger errors.

The expressions used in this report are:

Rate of loss = V ml./min./atm. pressure drop across tubing wall

$$W = \frac{V}{d}$$

where d is the length of tubing in cm., and W the rate of loss per centimetre length of tubing.

$$Y = \frac{V}{A}$$

where A is the area of the tubing in square centimetres and Y the rate of loss per square centimetre of internal area of tubing.

$Z = Yl$ where Z is rate of loss per square centimetre of internal area per mm. of wall thickness. The difference in the partial pressure of the test gas on the two sides of the tubing wall is assumed to be one atmosphere in the case of pure non-atmospheric gases. Thus $P = KZ$, where P is Barrer's permeability constant and K is a dimensionless numerical constant to permit comparison of annular with plane sections, and contains a factor of 1/76 for comparison of unit pressure gradient and 1/60 for comparison of unit time.

The permeability rates of different gases to a single type of tubing vary over a wide range. A comparison of the ratio $\frac{Z(x)}{Z(H_2)}$ for hydrogen, carbon dioxide, ethane, ethylene, acetylene, propane, propene, *iso*butane, normal butane, *iso*butene, 1-butene, 2-butene, and mixed normal butenes is

Table I.

Permeability Rates for Hydrocarbon Gases through Pure Gum Rubber Tubing.

TABLE I.

Permeability Rates for Hydrocarbon Gases through Pure Gum Rubber Tubing.

Tubing.	Gas.	$W_{10} \times 10^3$.	$W \times 10^3$.	$Y_{10} \times 10^3$.	$Y \times 10^3$.	$Z \times 10^3$.	l.	H_2 Ratio.	i-C_4H_{10} Ratio.
Adams Supreme. 4 mm. I.D., 7·5 mm. O.D. Amber. S.G.* $= \frac{25°}{25°} = 0{\cdot}9153$.	H_2	0·298	0·233	0·242	0·189	0·0320	1·69	1·00	—
	CH_4	0·397	0·105	0·326	0·0863	0·0156	1·81	0·49	—
	CO_2	2·99	0·610	2·56	0·525	0·0913	1·74	2·85	—
	C_2H_2	4·76	0·643	3·99	0·540	0·0962	1·78	3·01	—
	C_2H_6	4·56	0·571	3·40	0·423	0·0755	1·78	2·36	—
	C_2H_4	2·79	0·499	2·24	0·404	0·0714	1·77	2·23	—
	C_3H_8	9·22	1·204	7·53	0·984	0·1873	1·90	5·85	—
	C_3H_6	7·22	1·322	6·03	1·117	0·2206	1·97	6·90	—
	i-C_4H_{10}	18·04	0·843	15·82	0·737	0·1433	1·94	4·48	—
Adams Supreme. 4 mm. I.D., 7·5 mm. O.D. Amber. S.G.* = 0·9151.	n-C_4H_8	64·3	14·04	54·4	11·9	2·176	1·83	68·0	—
	n-C_4H_8	62·7	14·57	51·6	12·0	2·184	1·82	68·3	3·90
	C_4H_8-1	52·5	12·43	40·6	9·62	1·761	1·83	55·0	3·14
	C_4H_8-2	89·2	18·90	71·2	15·1	2·688	1·78	84·0	4·80
Adams Supreme. 4 mm. I.D., 7·5 mm. O.D. Amber. S.G.* = 0·9089.	i-C_4H_8	36·1	12·14	26·3	8·83	1·690	1·91	52·8	3·06
	n-C_4H_8	57·7	14·40	42·4	10·65	1·845	1·73	57·7	3·34
	i-C_4H_{10}	20·0	4·30	15·5	3·30	0·552	1·67	17·3	1·00
	n-C_4H_{10}	56·1	14·70	44·2	11·54	2·157	1·87	67·4	3·91
	C_4H_8-2	—	15·49	—	12·35	2·201	1·78	68·8	3·99
Adams Supreme. 4 mm. I.D., 7·5 mm. O.D. Amber. S.G.* = 0·9089.	i-C_4H_8	40·7	11·71	29·5	8·46	1·545	1·83	48·3	2·73
	n-C_4H_8	88·6	22·21	64·9	16·28	2·824	1·78	88·3	4·99
	i-C_4H_{10}	18·9	4·43	14·5	3·40	0·566	1·66	17·7	1·00
	n-C_4H_{10}	63·3	14·83	49·9	11·65	1·993	1·71	62·3	3·52

W_{10} and Y_{10} denote values for the first 10 minutes of the test.
W and Y are the normal values for the test. All values were obtained at room temperatures of 75–80° F.

H_2 ratio $= \frac{Z(x)}{Z(H_2)}$, where x is a given gas tested on the same type of tubing.

*iso*Butane ratio $= \frac{Z(x)}{Z(i\text{-}C_4H_{10})}$, where x is a given gas tested on the same type of tubing.

l = Average wall thickness in mm. The I.D. and O.D. values are the manufacturers', and are approximate only.
S.G.* = Specific gravity.

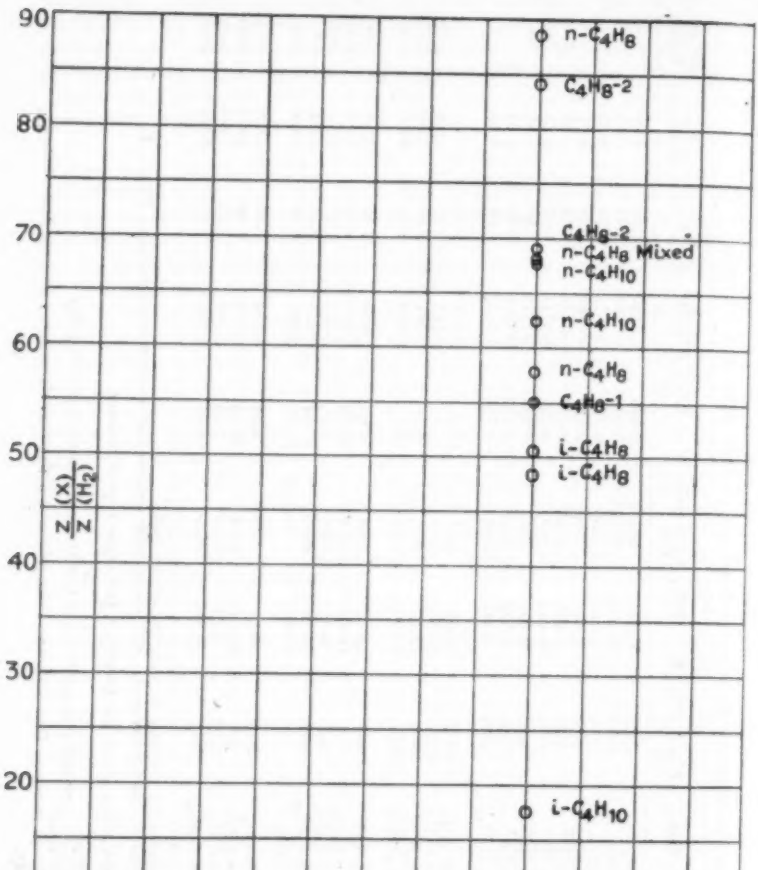

FIG. 1.

DIFFERENCES IN PERMEABILITY OF AMBER PURE GUM RUBBER TUBING (4 MM. ID., 7·5 MM. O.D.) TO VARIOUS GASES.

represented in Fig. 1; x represents the various pure gases studied. No other sample was tested with as many gases.

Pure gases maintained steady rates of loss and left no residual volumes. Gases containing traces of inert impurities tended to lose volume at a diminishing rate. This diminution was minimized by flushing the rubber tube after each reading—that is, by rolling the tubing to expel the gas in the tubing into the burette and releasing.

Interpretation of Data.

In estimating the permeability rate, it was found possible to correct for the presence of inert impurities. Various rates of gas loss and the mean volume of gas remaining corresponding to these rates were determined. A curve was plotted showing various rates versus the quantity

$$\frac{V \text{ total} - V \text{ inert}}{V \text{ total}}$$

i.e., the equivalent partial pressure of active gas in remaining gas, for several assumed values of V inert. The resultant curves were generally straight lines. That curve which passed through the line, Partial Pressure of gas = 0, at zero rate, was assumed to indicate the true value of inert gas. The extrapolation of this curve to the line, Partial Pressure of gas = 1 atm. —*i.e.*, 100 per cent. active gas—was taken to give the rate for the pure gas.

Variation of Losses with Time.

In the permeation of rubber by gas of constant composition to a region also containing a gas of constant composition, the conditions approximated in these experiments, a steady state of flow and a static concentration gradient, are reached. Before attaining the steady state, the rate of influx of permeating gas at one surface is greater than the rate of efflux at the other. During the steady state, the rate of influx and efflux are equal, and intermediate to the initial values. This indicates that a fresh piece of rubber tubing will cause greater gas losses than a piece of tubing in contact with the gas for a longer time. For this reason W and Y values were computed on the gas loss occurring in the first 10 minutes of each experiment. These values are tabulated and compared in Table II. To determine the gas loss for a given tubing in the region of room temperature, find the appropriate value for W and insert with it the proper values in the formula: Gas loss = $Wd \,.\, pT$, where d is length of tubing in centimetres, p is the difference in partial pressure of the permeating gas on both sides of the tubing in atmospheres and T is the time in minutes.

Relation of Composition of Rubber to Absolute Permeability.

It has already been reported that the compounding ingredients in rubber or Neoprene may either greatly reduce or increase the permeating power of a gas.[7] It is also reported that the curing time, age, and state of oxidation of a sample of rubber change its permeability. The significance of comparisons of data for samples from different batches of tubing is, consequently,

TABLE II.

Permeability of Rubber Tubings by Butanes and Butenes.

Tubing.	Gas.	$W_{10} \times 10^3$.	$W \times 10^3$.	$Y_{10} \times 10^3$.	$Y \times 10^3$.	$Z \times 10^3$.	l.	*i*-Butane Ratio.
"Cenco" Amber.	*i*-C_4H_8	36·7	9·5	25·2	6·50	1·06	1·63	2·86
$\frac{1}{16}$ in. I.D., $\frac{1}{8}$ in. O.D.	*n*-C_4H_8	65·0	15·1	43·9	10·18	1·66	1·63	4·49
S.G.* = 0·9451.	*i*-C_4H_{10}	16·1	3·3	10·8	2·25	0·37	1·64	1·00
	n-C_4H_{10}	50·2	9·9	34·0	6·60	1·09	1·65	2·95
"Cenco" Pure Gum Amber.	*i*-C_4H_8	62·7	12·4	31·6	6·26	1·02	1·63	4·85
Medium Wall Extruded.	*n*-C_4H_8	65·3	24·9	33·4	12·77	2·05	1·61	9·76
$\frac{1}{4}$ in. I.D., $\frac{3}{8}$ in. O.D.	*i*-C_4H_{10}	—	2·7	—	1·38	0·21	1·52	1·00
S.G.* = 0·9395.	*n*-C_4H_{10}	81·6	19·0	41·5	10·74	1·50	1·40	7·14
U.S. Rubber Co. Red Rubber.	*i*-C_4H_8	44·0	9·2	29·5	6·19	0·69	1·11	2·65
Cloth Finish, Thin Wall.	*n*-C_4H_8	65·3	8·5	43·7	5·69	0·66	1·16	2·54
$\frac{1}{16}$ in. I.D., $\frac{1}{8}$ in. O.D.	*i*-C_4H_{10}	19·0	3·3	12·7	2·24	0·26	1·16	1·00
S.G.* = 1·097.	*n*-C_4H_{10}	44·0	9·1	29·5	6·03	0·70	1·16	2·70
U.S. Rubber Co. Red Rubber.	*i*-C_4H_8	52·5	10·3	26·7	5·26	0·90	1·71	2·50
Cloth Finish, Thin Wall.	*n*-C_4H_8	—	13·1	—	6·75	1·12	1·66	3·11
$\frac{1}{4}$ in. I.D., $\frac{3}{8}$ in. O.D.	*i*-C_4H_{10}	17·4	4·3	8·8	2·20	0·36	1·64	1·00
S.G.* = 1·108.	*n*-C_4H_{10}	70·5	10·7	35·5	5·39	0·87	1·62	2·42
U.S. Rubber Co. Red Rubber.	*i*-C_4H_8	19·6	4·4	19·7	4·50	1·47	3·27	2·53
Cloth Finish, Pressure.	*n*-C_4H_8	23·0	6·5	23·3	6·55	2·14	3·27	3·69
$\frac{1}{4}$ in. I.D., $\frac{3}{8}$ in. O.D.	*i*-C_4H_{10}	14·1	1·8	14·3	1·80	0·58	3·22	1·00
Style 831. S.G.* = 1·104.	*n*-C_4H_{10}	27·9	4·5	27·6	4·45	1·46	3·28	2·52
U.S. Rubber Co. Red Rubber.	*i*-C_4H_8	34·1	8·5	22·6	5·74	1·87	3·26	2·60
Cloth Finish, Pressure.	*n*-C_4H_8	73·5	12·7	49·2	8·51	2·73	3·21	3·79
$\frac{1}{16}$ in. I.D., $\frac{1}{8}$ in. O.D.	*i*-C_4H_{10}	15·4	3·3	10·3	2·21	0·72	3·26	1·00
Style 831. S.G.* = 1·098.	*n*-C_4H_{10}	44·3	8·9	30·1	6·03	2·01	3·33	2·79
		45·0	11·5	34·1	6·03	2·17	3·60	2·36

U.S. Rubber Co. Red Rubber.	i-C_4H_8	45·9	11·5	24·1	6·03	2·17	3·60	2·36
Cloth Finish, Pressure.	n-C_4H_8	96·1	21·4	49·0	10·87	3·85	3·54	4·18
$\frac{1}{4}$ in. I.D., $\frac{1}{2}$ in. O.D.	i-C_4H_{10}	19·0	4·8	9·9	2·55	0·92	3·61	1·00
S.G.* = 1·108.	n-C_4H_{10}	57·4	12·5	29·7	6·48	2·38	3·67	2·59
Neoprene (Cenco).	i-C_4H_8	9·5	0·38	6·4	0·256	0·040	1·56	3·08
Cloth Finish, Black.	n-C_4H_8	20·0	1·32	13·6	0·905	0·142	1·57	10·92
$\frac{1}{16}$ in. I.D., $\frac{1}{16}$ in. O.D.	i-C_4H_{10}	2·6	0·11	1·8	0·077	0·013	1·69	1·00
S.G.* = 1·393.	n-C_4H_{10}	6·5	0·35	5·8	0·240	0·038	1·58	2·77
Neoprene (Cenco).	i-C_4H_8	10·8	0·83	5·4	0·421	0·102	2·42	3·52
Cloth Finish, Black.	n-C_4H_8	25·6	2·61	12·8	1·324	0·317	2·39	10·93
$\frac{1}{4}$ in. I.D., $\frac{7}{16}$ in. O.D.	i-C_4H_{10}	3·3	0·28	1·6	0·126	0·029	2·30	1·00
S.G.* = 1·392.	n-C_4H_{10}	13·1	0·96	6·6	0·439	0·111	2·53	3·83
Electric Cable Casing.	i-C_4H_8	0·46	0·44	0·26	0·245	0·024	0·98	6·00
"Synthetic Rubber, Oil Proof."	n-C_4H_8	1·51	1·07	0·84	0·593	0·061	1·03	15·25
6 mm. I.D., 8 mm. O.D.	i-C_4H_{10}	0·13	0·08	0·08	0·041	0·004	0·93	1·00
S.G.* = 1·630.	n-C_4H_{10}	0·89	0·30	0·48	0·171	0·017	0·99	4·25
Goodrich Koroseal. S.G.* Grade.								
$\frac{3}{16}$ in. I.D., $\frac{1}{4}$ in. O.D. 1·254 673	C_4H_8·2	35·1	3·9	22·2	2·46	0·396	1·61	—
$\frac{1}{4}$ in. I.D., $\frac{3}{8}$ in. O.D. 1·254 673	C_4H_8·2	42·7	6·4	20·5	3·06	0·560	1·83	—
$\frac{3}{16}$ in. I.D., $\frac{7}{16}$ in. O.D. 1·404* 1119	C_4H_8·2	20·3	3·1	12·5	1·90	0·601	3·16	—
Resistoflex.	n-C_4H_8	0·018	0·0068	0·0065	0·00271	0·00037	—	1st 10 days
7 mm. I.D. × 10 mm. O.D.	—	—	0·0030	—	0·00114	0·00016	1·40	2 weeks on
Paraffin Impregnated.								
Red $\frac{1}{4}$ in. × $\frac{3}{8}$ in.	n-C_4H_8	64·9	31·7	28·7	13·3	2·68	2·02	—
Red $\frac{1}{4}$ in. × $\frac{1}{2}$ in.	n-C_4H_8	108·9	40·4	51·1	18·4	4·98	2·71	—
Cenco Amber $\frac{1}{4}$ in. × $\frac{3}{8}$ in.	n-C_4H_8	97·1	37·4	44·9	17·9	3·20	1·79	—

l = Average wall thickness in mm.

S.G.* = Specific gravity.

somewhat uncertain. A comparison was made of Z for C_4 gases for samples from three different kinds of tubing. Fig. 2 presents graphically the data for various amber pure gum samples of several radii; Fig. 3 for thin-walled and pressure-type red rubber tubing; and Fig. 4 for chloroprene base tubing (Neoprene) and Koroseal.

Four gases—*iso*butane, normal butane, *iso*butene and a mixture of the normal butenes—were tested on a large variety of standard and pressure

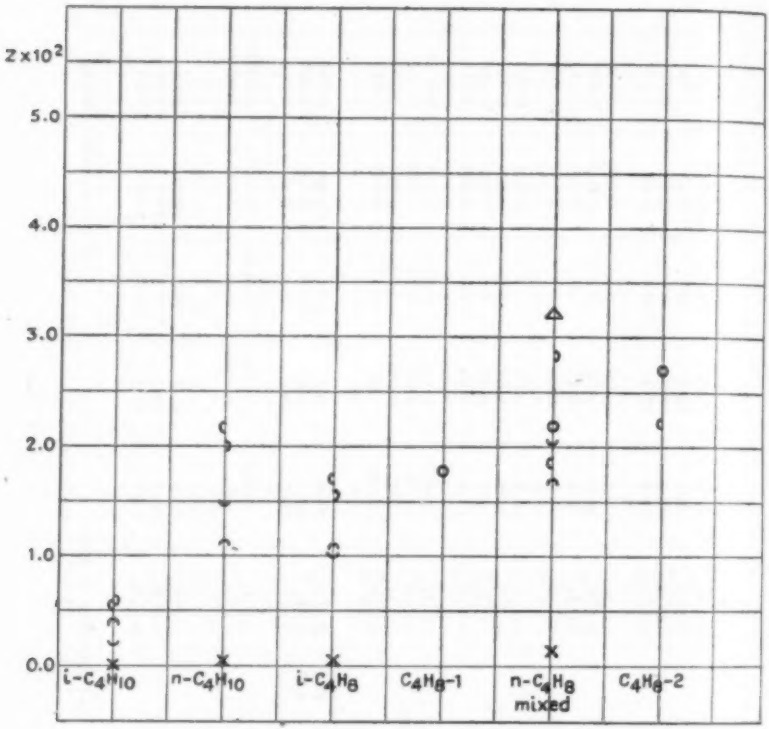

FIG. 2.

RELATION OF COMPOSITION OF RUBBER TO ABSOLUTE PERMEABILITY: GUM RUBBER.

tubings made from natural rubber, and on a limited number of samples of Neoprene and Koroseal. These data are tabulated in Table II.

RELATION OF COMPOSITION OF RUBBER TO RELATIVE PERMEABILITY.

The ratio $\frac{Z(x)}{Z(i\text{-}C_4H_{10})}$ in Fig. 5 illustrates the fact that differences in permeability may vary from material to material. The differences in Z for pure gum and compound rubber were large (Figs. 2 and 3). The

ratios were very similar. The chloroprene-base samples show a marked similarity among themselves, but a very considerable difference from rubber.

General Conclusions.

Error in Gas Analysis Due to Rubber.

The contact of gases with rubber may result in change in the quantity and composition of the gas. If rubber tubing is interposed between a

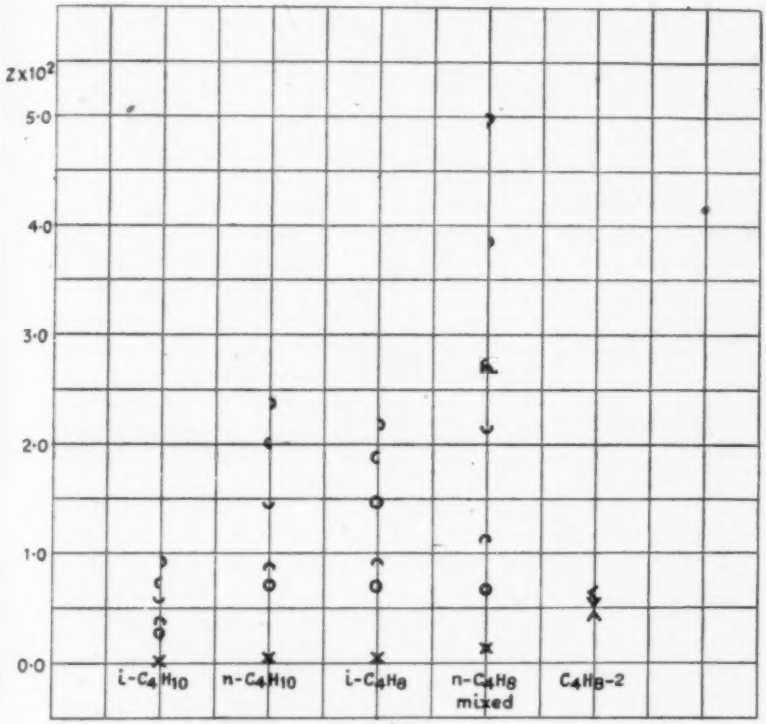

Fig. 3.

Relation of composition of rubber to absolute permeability: red rubber.

flow meter and a plant, the space velocity calculated for the plant will be in error. The percentage error will be an inverse function of the rate and a direct function of the length of the tube.

If a sample is conducted from a plant to a gas-collecting bottle or tube, the composition will undergo change. If the tubing is short, if the components are of like permeating power, and the period of collection is short, the error will be negligible; but if the components differ widely in permeating power, and the sample is left connected to the tubing for a long

period, as frequently happens in taking composite samples, the error will be practically unlimited. If a manifold in a gas analytical apparatus contains excessive amounts of rubber, it will not only dissolve components present in high concentration, but will subsequently liberate them, causing an error in the next operation or analysis. It is also apparent that if a gas containing components of widely different permeating power is stored

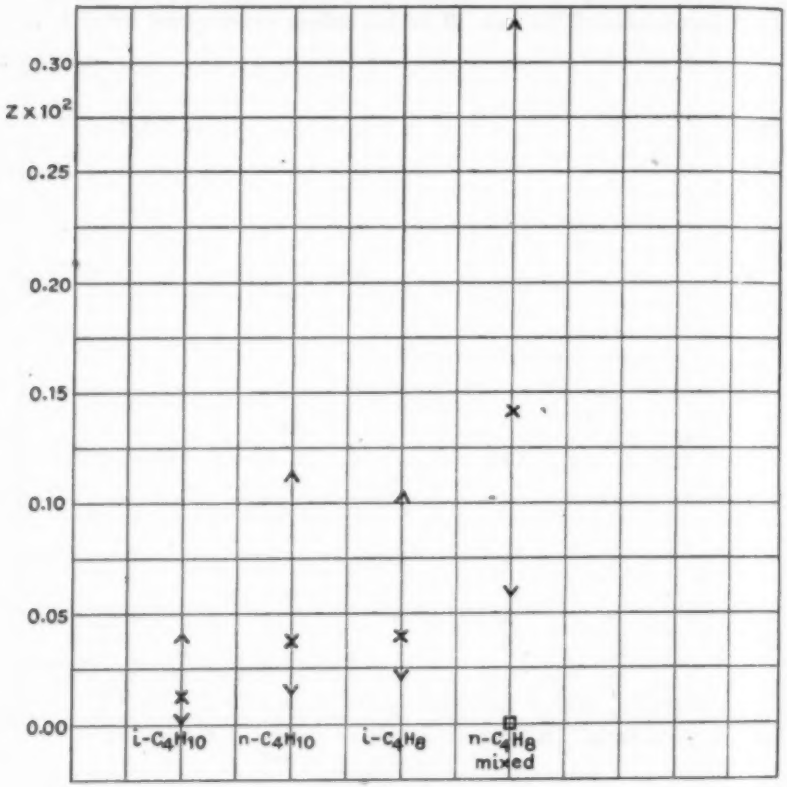

FIG. 4.

RELATION OF COMPOSITION OF RUBBER TO ABSOLUTE PERMEABILITY: SYNTHETIC RUBBER.

in a rubber-stoppered container, its composition will gradually change until each component is present in inverse proportion to its permeating power.

Table III shows an example of change of composition of a gas when sampled through a 200-cm. length of 4 mm. I.D., 7·5 mm. O.D., gum-rubber tubing. The following assumptions were made: A 10-hour composite, 5-litre sample of gas of composition #1 was passed through the

length of tubing at a rate of 25 ml./3 minute periods. The internal volume of the rubber tubing was 25·13 ml. Thus each portion of gas passing through the tubing was in contact with it for approximately three minutes.

W = gas loss in ml./min./atm./cm. length of tubing, so that gas loss

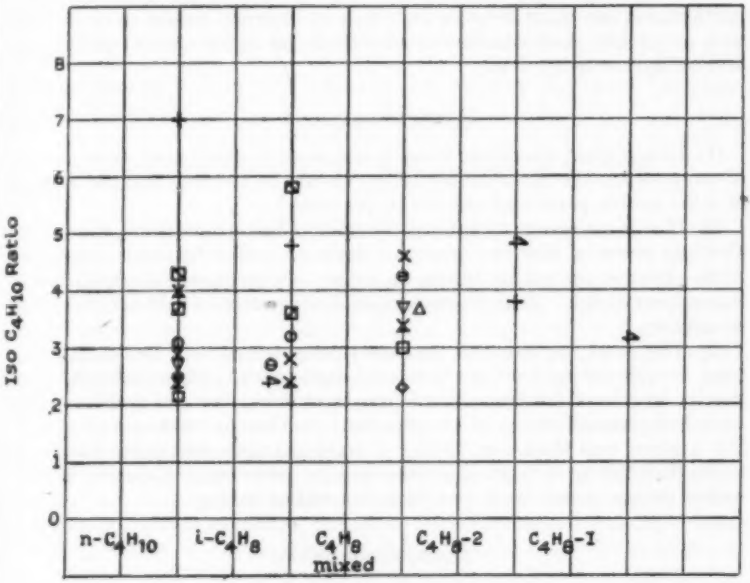

FIG. 5.

iso-BUTANE RATIO $\frac{Z(x)}{Z(i\text{-}C_4H_{10})}$

TABLE III.

Effect of Variations in Permeability Rates on Hydrocarbon Composition.

Component.	Analysis, mole. %.	Original Volume, ml.	Gas Loss, ml.	Corrected Volume, ml.	Final Composition, mole. %.
Hydrogen . .	17·2	4·30	0·024	4·276	22·3
Air . . .	0·7	0·175	0·139	0·314	1·6
Methane . .	1·8	0·45	0·001	0·449	2·3
Propylene . .	1·0	0·25	0·008	0·242	1·3
Propane . .	5·9	1·475	0·043	1·432	7·5
iso-Butylene .	5·3	1·325	0·372	0·953	5·0
n-Butylene . .	10·5	2·625	1·399	1·226	6·4
iso-Butane . .	16·0	4·00	0·425	3·575	18·6
n-Butane . .	41·6	10·40	3·694	6·706	35·0
	100·0	25·00	5·827	19·173	100·0

in ml. $= W \times$ minutes $\times$ atmospheres $\times$ cm. length. For example: Hydrogen loss $= 0{\cdot}233 \times 10^{-3} \times 3 \times \frac{17{\cdot}2}{100} \times 200 = 0{\cdot}024$ ml. in 25 ml. of effluent gas. The partial pressure of hydrogen in the gas is equivalent to the per cent. of hydrogen divided by 100. It will be noted that the balance between hydrogen and olefins is entirely destroyed. A similar disproportionation can occur between *iso*butane and normal butane in operations such as cracking, isomerization or alkylation, giving erroneous equilibrium, and catalyst activity data.

Recommendations.

(1) In any plant operation where it is desired to avoid gas loss or change of composition, the use of rubber tubing should be avoided, and the contact of other rubber parts with the gas be prevented.

(2) If it is necessary to have easily opened line connections, the use of abutting pieces of glass or copper in a sleeve of rubber tubing is suggested. *Note.*—Do not use rubber tubing on copper connections if the installation is semi-permanent. Copper causes rapid deterioration of rubber by removal of sulphur.

(3) The most impermeable flexible tubing tested was Resistoflex. If long, flexible tubing lines are necessary, Resistoflex is recommended. For shorter lengths of flexible tubing in gas-tight lines, Koroseal and Neoprene have low permeabilities and are superior to rubber in resistance to ageing. For a given wall thickness, tubing of small diameter will cause lower gas losses than tubing of larger diameter, and for given inside diameter, heavy-walled tubing causes lower loss than thin-walled tubing.

Acknowledgments.

The authors wish to express their appreciation to Miss E. E. Crandal, Dr. C. L. Thomas, Dr. G. M. Webb, and Mr. C. G. Dryer for reviewing the manuscript.

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THE CALCULATION OF THE VOLUMES CONTAINED IN THE PARTIALLY FILLED DISH ENDS OF HORIZONTAL CYLINDRICAL TANKS.

By H. A. Blackmore.* (Fellow.)

The volume of a spherical segment bounded by one curved and one plane surface is given by :

$$v = \tfrac{1}{3}\pi d^2(3R - d) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where R = radius of sphere and d = height of segment,
and by :

$$v = \tfrac{1}{6}\pi d(d^2 + 3r^2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where r = radius of base of segment.

The figures representing the volumes of liquid contained in the dish ends of horizontal cylindrical tanks, except when these are full, are formed by the interception, by the plane surface of the liquid, of the dish end and an imaginary plane which would constitute the end of the tank if this were flat. These figures are therefore bounded by three surfaces; two plane and one curved, and the angle between the plane surfaces is 90° when the axis of the cylinder is horizontal. The above equations therefore apply only to the full dish end.

Since oil volumes are calculated from the heights of oil in the tanks, measured by dipping, h must be the independent variable and, in order to obtain a rigorous equation, the other variables must be changed into explicit functions of h. However, such a function is, within the author's experience, intractable and probably, if integrable, would be useless for ordinary work owing to its complexity.

In an attempt to overcome this difficulty, it was assumed that certain angular functions were substantially invariant with h in so far as these could be measured from the tank blue print, and an equation was derived

$$v = (\theta - \sin\theta \,.\, \cos\theta)\left(\frac{h^3}{3\tan\phi} + \frac{h^2 z}{\tan\phi} + hz^2\right)$$

where h = height of liquid,
z = radius of curvature—depth of dishing,
θ = half the angle subtended by the arc which the surface of the liquid forms in the dish end,
ϕ = the angle between the liquid level and a chord drawn from its point of interception with the dish end to the point of interception of the dish end with the bottom centre line of the cylinder.

This equation, however, gave results which were too high when checked against equations (1) and (2) for a completely filled dish end, and an

* *Note.*—In the absence of the author abroad this paper has been seen through the Press by Dr. G. D. Hobson.

attempt to correct this by taking average graphical values for θ and ϕ between $h = h$ and $h = 0$ gave results which were too low.

The simplifying assumption was therefore made that the dish ends are not spherical, but are segments of a paraboloid of revolution, which leads to more tractable integrals. The error thus introduced will be shown to be negligible for practical purposes. It can be corrected if desired.

Fig. 1 shows the parabolic segment a ft. below the axis of the tank.

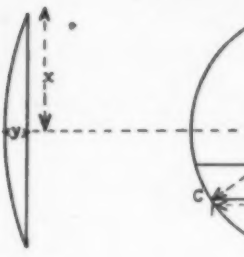

FIG. 1.

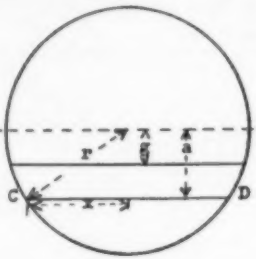

FIG. 2.
SECTION THROUGH AB.

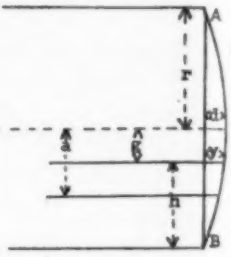

FIG. 3.
VERTICAL SECTION THROUGH AXIS.

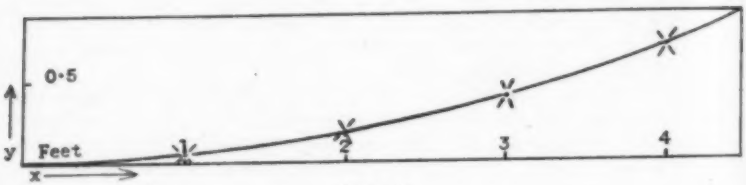

FIG. 4.

We have:

$$y = kx^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now when $a = 0$, $y = d$ (depth of dish), and $x = r$ (radius of cylinder),

$$\therefore \quad k = \frac{d}{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

And the equation of the parabola is:

$$y = \frac{d}{r^2} \cdot x^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Fig. 4 is a scale drawing (1½ in. to 1 ft.) of the curve of the dish end of a 30 ft. × 9 ft. horizontal cylindrical tank, between the axis and the side of the cylinder. The points on the curve are the intersections of the x and y co-ordinates, the values of y being obtained from equation (5).

The area of the parabolic segment (Fig. 1) is:

$$\frac{4}{3}xy = \frac{4}{3}\frac{d}{r^2}x^3 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

But from Fig. 2 it is seen that :

$$x = (r^2 - a^2)^{\frac{1}{2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\therefore \quad \text{area of segment} = \frac{4\,d}{3\,r^2}(r^2 - a^2)^{\frac{3}{2}} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

and the volume of liquid in the dish end to a depth $h = r - g$ is :

$$\frac{4\,d}{3\,r^2}\int_{a=g}^{a=r}(r^2 - a^2)^{\frac{3}{2}}da \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$= \frac{4\,d}{3\,r^2}\left[\frac{a}{8}(5r^2 - 2a^2)\sqrt{r^2 - a^2} + \frac{3r^4}{8}\,.\,\sin^{-1}\frac{a}{r}\right]_g^r \quad . \quad . \quad . \quad (10)$$

When $a = r$ the first term vanishes and the second reduces to $\frac{3r^4}{8}\cdot\frac{\pi}{2}$.

Thus we get :

$$\text{Volume} = \frac{4\,d}{3\,r^2}\left[\frac{3r^4}{8}\left(\frac{\pi}{2} - \sin^{-1}\frac{g}{r}\right) - \frac{g}{8}(5r^2 - 2g^2)\sqrt{r^2 - g^2}\right] \quad . \quad (11)$$

$$= \tfrac{1}{2}dr^2\left(\frac{\pi}{2} - \sin^{-1}\frac{g}{r}\right) - \frac{1}{6}\frac{dg}{r^2}(5r^2 - 2g^2)\sqrt{r^2 - g^2} \quad . \quad . \quad (12)$$

where r is the radius of the base of the dish end (*i.e.*, radius of horizontal cylindrical tank),

d is the depth of the dishing, assumed parabolic,

g is the height of the axis above the liquid surface (*i.e.*, $g = r - h$, if h is the depth of liquid in the tank).

This assumption leads to results about 1 per cent. low when r is about five times d, the usual ratio, owing to the difference between a segment of a sphere and one of a paraboloid of revolution. The difference for other ratios of r to d can be roughly computed as follows.

Spherical segment $= \frac{1}{6}\pi d(d^2 + 3r^2) = \frac{1}{2}\pi dr^2 + \frac{1}{6}\pi d^3$.

Paraboloidal segment $= \frac{1}{2}\pi dr^2$.

Hence the proportional excess of the spherical over the paraboloidal segment is :

$$\tfrac{1}{6}\pi d^3/\tfrac{1}{2}\pi dr^2 = d^2/3r^2 \text{ or } 33{\cdot}3\ d^2/r^2\%.$$

The percentage error, calculated on the quantity of liquid in the dish, may be rather greater than this when the tank is less than half full, but the percentage calculated on the total capacity of the dish will never exceed this amount. If thought necessary, a correction can easily be applied by means of the above formula. For a 30 ft. × 9 ft. tank with a dish end of radius of curvature of 12 ft. (giving $d = \frac{7}{8}$ ft.) the error is only 0·17 cu. ft. per dish end when full, a negligible amount.

The following examples illustrate the method as applied to a 30 ft. × 9 ft. horizontal tank of a radius of curvature of 12 ft.

r = radius of base of segment = radius of cylinder = 4·5 ft.

d = 0·875 ft. (from Fig. 4). d is also given by :

$d = R - \sqrt{R^2 - r^2} = 12 - \sqrt{12^2 - 4{\cdot}5^2} = 0{\cdot}875$ ft., where R = radius of curvature of dish end and r = radius of cylinder.

$h = 2{\cdot}5$ ft. $\therefore\ g = 2$ ft.

Whence the volume contained in the two dish ends of the tank for a dip of 2·5 ft. would be approximately :

$$2[\tfrac{1}{2} \times 0{\cdot}875 \times 20{\cdot}25(1{\cdot}57 - \sin^{-1} 0{\cdot}444) - \frac{1}{6}\frac{(0{\cdot}875 \times 2)}{20{\cdot}25} \times (101{\cdot}25 - 8)\sqrt{20{\cdot}25 - 4}]$$
$$= 2[8{\cdot}86(1{\cdot}57 - 0{\cdot}46) - 0{\cdot}0144 \times 93{\cdot}25 \times 4{\cdot}03] = 2(9{\cdot}84 - 5{\cdot}42)$$
$$= 8{\cdot}84 \text{ cu. ft.}$$

The correction for "spherical error" $= 2 \times \frac{1}{3} \times \frac{0{\cdot}875^2}{4{\cdot}5^2} \times 4{\cdot}42 = 0{\cdot}12$ cu. ft.

Hence the corrected volume = 8·96 cu. ft.

Similarly the volume of liquid contained in one of the dish ends when $h = 4{\cdot}5$ ft. and $g = 0$ is :

$$\tfrac{1}{2} \times 0{\cdot}875 \times 20{\cdot}25(1{\cdot}57 - \sin^{-1} 0) = 13{\cdot}91 \text{ cu. ft.}$$

since the second term vanishes.

The correction for the error arising from the departure of the paraboloidal segment from the spherical segment will be :

$$\frac{1}{3}\frac{d^2}{r^2} \cdot 13{\cdot}91 = \frac{0{\cdot}875^2}{3 \times 4{\cdot}5^2} \cdot 13{\cdot}91 = 0{\cdot}18 \text{ cu. ft.}$$

Hence the corrected volume of the liquid in the dish, when $h = 4{\cdot}5$ ft., is 14·09 cu. ft. This result may be confirmed by calculating the volume of liquid by means of equations (1) or (2).

ANNUAL GENERAL MEETING.

Friday, 28th April, 1944.

The Thirty-first Annual General Meeting of the Institute was held at Manson House, 26, Portland Place, W.1, on Friday, 28th April, 1944, when Professor F. H. Garner, President, occupied the Chair.

The Secretary read the Notice convening the Meeting.

The Minutes of the Thirtieth Annual General Meeting were read, confirmed and signed.

Vice-Presidents.

The President reported that Messrs. Ashley Carter, G. H. Coxon, A. C. Hartley, V. C. Illing and J. S. Jackson had been elected Vice-Presidents.

Election of Members of Council.

The President: In accordance with the By-Laws the following members of Council retire but are eligible for re-election:

Messrs. E. A. Evans, A. Beeby Thompson, C. A. P. Southwell, and C. W. Wood.

Nominations in favour of Messrs. H. Hyams and Richard R. Tweed have also been received, and I propose that all these be elected members of Council.

The proposal was seconded by Lt.-Col. S. J. M. Auld and carried unanimously.

New Members.

It was agreed that the list of Fellows, Members, Associate Members and Students elected and transferred during 1943 should be laid on the table.

Adjournment of Meeting.

The President: The Council decided to hold the Annual General Meeting at the normal time although it was realized that the Accounts would not be ready. I therefore propose that this meeting be adjourned until such time as the Council may decide, of which due notice will be given. The Accounts and Annual Report of Council will be presented at this adjourned meeting.

Mr. C. A. P. Southwell seconded the proposal, which was carried unanimously.

Vote of Thanks.

Mr. T. Dewhurst: I am sure it will meet with your wish that we should give a hearty vote of thanks to our President for taking the Chair to-day

but, in doing so, I think we ought also to thank him for so kindly undertaking the duties in the interim period following the death of Mr. C. Dalley. I may say that during that brief period he has exhibited the qualities that we associate with the position of the Chair in a most excellent manner. We now have him in the Chair and I am sure you would like to wish him a very successful year of office.

DR. A. E. DUNSTAN seconded the proposal, which was carried unanimously.

The meeting then terminated.